

**Review of the PhD thesis “Crystal Chemistry of Natural Layered Double Hydroxides” submitted by Elena S. Zhitova for the degree of Doctor of Philosophy in Geology at the St.-Petersburg State University, Russia**

The dissertation of Elena Zhitova is characterized by clear statement of thesis topic, felicitous choice of subject of inquiry and reliability of obtained results. The theme of the thesis is dedicated to the studying one of the most enigmatic phenomenon in crystal chemistry – polytypism. Objects of inquiry in this dissertation are quintinite group minerals which came from deposits located in Kola Peninsula and Urals (Russia). Reliable results were provided by professional applying of modern X-ray structure analysis for solutions of four different crystal structures.

The first dissertator achievement is ascription of four studied mineral species to quintinite polytypes, despite of existing view that is belongs to manasseite and hydrotalcite groups.

Another shining attainment is detection of two new polymorphic modifications of quintinite among studied natural samples.

Largely both these nontrivial results were obtained due to progress in studying  $^{+} \text{ и } ^{+}$  ordering. Methodological difficulty lay in the fact that these cations have almost the same amount of electrons therefore their scattering factors are very close. In this situation analysis of «magnesium-oxygen» and «aluminum-oxygen» bond lengths proved to be highly effective. Significant difference in bond length, which has been detected in this work, allowed to establish unambiguously: ordering of cations on distinct crystallographic sites in  $2H-3c[6R]$ ,  $1M$ ,  $2H-1c$  polytypes of quintinite and disordered cations distribution in quintinite- $2H$ .

Especially I would like to pay attention to author`s conclusion about cause of polytypes formation: “The observed disorder is probably the result of a higher temperature of formation of the  $2H$  polytype compared with the ordered polytypes” (p. 14).

The opponent has the following request. On the page of dissertation is written: “The effect of cation ordering in natural LDHs with  $^{+} = ^{+}$  and  $^{+} = ^{+}$  is governed by the tendency to minimize  $^{+} - ^{+}$  repulsive interaction, what is energetically favored and in agreement with the cation avoidance rule (Lowenstein, 1954; Trave *et al.*, 2002)”. It should be mentioned, that cited rule is a particular case of one of five Poling`s rules. These rules have been proposed by Poling a quarter of a century before Lowenstein`s publication and still stay actual and relevant to our time. Due to this reason this rule should bear Poling`s name or names of both these outstanding scientists.

Results of work have been clearly stated in the thesis, fully presented in five articles and reported on different scientific conferences.

Received results on its completeness and reliability properly meet the requirements for PhD dissertations. Author of the thesis, Elena Zhitova, is worthy of the award of the PhD degree in Geology at St.-Petersburg State University.

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